JC03 Rec'd PCT/PTO 25 JUL 2001

FORM PTO-1390 (Rev. 12-29-99) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: 004900-200

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5): 09/889957

INTERNATIONAL APPLICATION NO.: PCT/FR00/00166

INTERNATIONAL FILING DATE: 25 January 2000

PRIORITY DATE CLAIMED: 25 January 1999

TITLE OF INVENTION: METHOD AND INSTALLATION FOR SEPARATING AND PURIFYING DIPHENOLS IN THE PHENOL AND PHENOL DERIVATIVES INDUSTRY

APPLICANT(S) FOR DO/EO/US: Jacques BOURDON; Daniel CLERIN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).

4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))

   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).

   b. ☒ has been transmitted by the International Bureau.

   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)

6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))

   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).

   b. ☐ have been transmitted by the International Bureau.

   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.

   d. ☐ have not been made and will not be made.

8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. ☒ A FIRST preliminary amendment.

    ☐ A SECOND or SUBSEQUENT preliminary amendment.

14. ☐ A substitute specification.

15. ☐ A change of power of attorney and/or address letter.

16. ☐ Other items or information:

09/889957 09889957 JC18 Rec'd PCT/PTO 25 JUL 2001

U.S. APPLICATION NO (If known, see 37 C.F.R. 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
09/889957	PCT/FR00/00166	004900-200

17. ☒ The following fees are submitted:	CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)):		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO $1,000.00 (960)		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO $860.00 (970)		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO $710.00 (958)		
International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) $690.00 (956)		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) $100.00 (962)		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00	
Surcharge of **$130.00 (154)** for furnishing the oath or declaration later than 20 ☐ 30 ☐ months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	20 -20 =	0	X$18.00 (966)	$ --	
Independent Claims	1 -3 =	0	X$80.00 (964)	$ --	
Multiple dependent claim(s) (if applicable)			+$270.00 (968)	$	
TOTAL OF ABOVE CALCULATIONS =				$ 860.00	
Reduction for 1/2 for filing by small entity, if applicable (see below).				$	-
SUBTOTAL =				$ 860.00	
Processing fee of **$130.00 (156)** for furnishing the English translation later than 20 ☐ 30 ☐ months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$ 860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00 (581)** per property +				$	
TOTAL FEES ENCLOSED =				$ 860.00	
				Amount to be: refunded	$
				charged	$

a. ☐ Small entity status is hereby claimed.

b. ☒ A check in the amount of $ 860.00 to cover the above fees is enclosed.

c. ☐ Please charge my Deposit Account No. 02-4800 in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

d. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4800. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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30,427
REGISTRATION NUMBER

Patent
Attorney's Docket No. 004900-200

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of	)
Jacques BOURDON et al.	) Group Art Unit: Unassigned
Application No.: Unassigned (Corresponds to PCT/FR00/00166	) Examiner: Unassigned
International Filing Date: 25 January 2000	)
For: METHOD AND INSTALLATION OR SEPARATING AND PURIFYING DIPHENOLS IN THE PHENOL AND PHENOL DERIVATIVES INDUSTRY	)

PRELIMINARY AMENDMENT

BOX PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-captioned application as follows:

IN THE CLAIMS:

Kindly amend the claims as follows:

Kindly replace claims 1-11 and 13-20 as follows.

1. (Amended) A process for separation and purification of a crude mixture comprising hydroquinone and resorcinol, optionally tars, and optionally catechol, in which process the crude mixture is first subjected to a series of distillation stages comprising:

(i) optionally distilling in stage (I) [designed] to produce catechol as a distillation top product,

(ii) obtaining the distillation bottom product from (i) or the crude mixture in the absence of stage (I) to a distillation stage (II) designed to produce, as

distillation a top product, a resorcinol-rich fraction comprising resorcinol and hydroquinone,

(iii) subjecting the distillation bottom product obtained from (ii) to a distillation stage (III) designed to produce, as a distillation top product, a hydroquinone-rich fraction comprising hydroquinone and resorcinol,

and then subjecting the hydroquinone-rich fraction and/or the resorcinol-rich fraction to a refining stage (IV or V) in order to extract the hydroquinone and/or the resorcinol respectively.

2. (Amended) The process as claimed in claim 1, wherein stage (I), when it is present, or stage (II) is preceded by at least one preliminary detarring stage (1, 1') designed to produce, as a bottom product, a tar-rich fraction and, as a top product, a detarred fraction which is used to feed stage (I) or stage (II).

3. (Amended) The process as claimed in claim 2, wherein two predistillation stages (1, 1') are provided, the tar-rich bottom fraction from the first (1) being used to feed the second (1') and the two detarred top fractions being used to feed stage (I) or (II).

4. (Amended) The process as claimed in claim 1, wherein stage (II) is designed to result in a resorcinol-rich fraction comprising:

- from 75 to 95% resorcinol, and
- from 5 to 25% hydroquinone.

5. (Amended) The process as claimed in claim 1, wherein stage (III) is designed to result in a hydroquinone-rich fraction comprising:

- from 75 to 98% hydroquinone, and
- from 2 to 25% resorcinol.

6. (Amended) The process as claimed in claim 1, wherein the refining of the rich fractions is carried out on drainers.

7. (Amended) The process as claimed in claim 1, wherein the distillation column (I) has the following specifications:

- number of theoretical stages: from 5 to 40; and
- reflux ratio R of between 1 and 10.

8. (Amended) The process as claimed in claim 1, wherein the distillation column (II) has the following specifications:

- number of theoretical stages: from 10 to 85; and
- reflux ratio R of between 1 and 35.

9. (Amended) The process as claimed in claim 1, wherein the distillation column (III) is a scraped falling film device or a distillation column having the following specifications:

- number of theoretical stages: from 1 to 10, and
- reflux ratio R of between 0.5 and 5.

10. (Amended) The process as claimed in claim 1, wherein the detarring column or columns (1, 1') is/are scraped falling film devices.

11. (Amended) The process as claimed in claim 1, wherein the crude mixture comprises, with respect to the total mixture:

- from 20 to 60% by weight of hydroquinone,
- from 2 to 20% by weight of resorcinol,
- from 0 to 20% by weight of catechol, and
- the remainder being formed of various compounds comprising tars.

13. (Amended) The plant as claimed in claim 12, which additionally comprises:

- a detarring column (1) designed to produce, at the column top, a detarred fraction and, at the bottom of the column, a tar-rich fraction
- optionally at least one other distillation column (11) fed with the tar-rich fraction originating from the preceding column (1) and designed to produce, at the column top, a detarred fraction and, at the bottom, a tar-rich fraction,

the top fraction or fractions of these columns being used to feed column (I) or (II).

14. (Amended) The plant as claimed in claim 12, wherein the column (II) is designed to result in a resorcinol-rich fraction comprising:

- from 75 to 95% resorcinol, and
- from 5 to 25% hydroquinone.

15. (Amended) The plant as claimed in claim 12, wherein the column (III) is designed to result in a hydroquinone-rich fraction comprising:

- from 75 to 98% hydroquinone, and
- from 2 to 25% resorcinol.

16. (Amended) The plant as claimed in claim 12, wherein the refining device or devices are drainers.

17. (Amended) The plant as claimed in claim 12, wherein the distillation column (I) has the following specifications:

- number of theoretical stages: from 5 to 40; and
- reflux ratio R of between 1 and 10.

18. (Amended) The plant as claimed in claim 12, wherein the distillation column (II) has the following specifications:

- number of theoretical stages: from 10 to 85[, preferably from 15 to 40; and reflux ratio R of between 1 and 35.

19. (Amended) The plant as claimed in claim 12, wherein the distillation column (III) is a scraped falling film device or a distillation column having the following specifications:

- number of theoretical stages: from 1 to 10, and
- reflux ratio R of between 0.5 and 5.

20. (Amended) The plant as claimed in claim 12, wherein the detarring column or columns (1, 1') is/are scraped falling film devices.

REMARKS

Entry of the foregoing amendments are respectfully requested.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: _____
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Date: July 25, 2001

Attachment to Preliminary Amendment dated July 25, 2001

1. (Amended) A process for separation and purification of a crude mixture comprising hydroquinone and resorcinol, optionally tars, and optionally catechol, in which process the crude mixture is first [of all] subjected to a series of distillation stages comprising:

(i) [an optional distillation] optionally distilling in stage (I) [designed] to produce catechol as a distillation top product,

(ii) obtaining the distillation bottom product [obtained under] from (i) or the crude mixture in the absence of stage (I) [is subjected] to a distillation stage (II) designed to produce, as distillation a top product, a resorcinol-rich fraction comprising resorcinol[, essentially,] and hydroquinone,

(iii) subjecting the distillation bottom product obtained [under] from (ii) [is subjected] to a distillation stage (III) designed to produce, as a distillation top product, a hydroquinone-rich fraction comprising hydroquinone[, essentially,] and resorcinol,

and then subjecting the hydroquinone-rich fraction and/or the resorcinol-rich fraction [is/are subjected] to a refining stage (IV or V) in order to extract the hydroquinone and/or the resorcinol respectively.

2. (Amended) The process as claimed in claim 1, [characterized in that] wherein stage (I), when it is present, or stage (II) is preceded by at least one preliminary detarring stage (1, 1') designed to produce, as a bottom product, a tar-rich fraction and, as a top product, a detarred fraction which is used to feed stage (I) or stage (II).

Attachment to Preliminary Amendment dated July 25, 2001

3. (Amended) The process as claimed in claim 2, [characterized in that] wherein two predistillation stages (1, 1') are provided, the tar-rich bottom fraction from the first (1) being used to feed the second (1') and the two detarred top fractions being used to feed stage (I) or (II).

4. (Amended) The process as claimed in [any one of claims 1 to 3] claim 1, [characterized in that] wherein stage (II) is designed to result in a resorcinol-rich fraction comprising:

- from 75 to 95%[, preferably from 85 to 92%, of] resorcinol, and
- from 5 to 25%[, preferably from 8 to 15%, of] hydroquinone.

5. (Amended) The process as claimed in [any one of claims 1 to 4] claim 1, [characterized in that] wherein stage (III) is designed to result in a hydroquinone-rich fraction comprising:

- from 75 to 98%[, preferably from 85 to 97.5%, of] hydroquinone, and
- from 2 to 25%[, preferably from 2.5 to 15%, of] resorcinol.

6. (Amended) The process as claimed in [any one of claims 1 to 5] claim 1, [characterized in that] wherein the refining of the rich fractions is carried out on drainers.

Attachment to Preliminary Amendment dated July 25, 2001

7. (Amended) The process as claimed in [any one of claims 1 to 6] claim 1, [characterized in that] wherein the distillation column (I) has the following specifications:

- number of theoretical stages: from 5 to 40[, preferably from 10 to 30]; and

- reflux ratio R of between 1 and 10[, preferably between 2 and 5].

8. (Amended) The process as claimed in [any one of claims 1 to 6] claim 1, [characterized in that] wherein the distillation column (II) has the following specifications:

- number of theoretical stages: from 10 to 85[, preferably from 15 to 40]; and
- reflux ratio R of between 1 and 35[, preferably between 5 and 25].

9. (Amended) The process as claimed in [any one of claims 1 to 6] claim 1, [characterized in that] wherein the distillation column (III) is a scraped falling film device or a distillation column having the following specifications:

- number of theoretical stages: from 1 to 10[, preferably from 1 to 5], and
- reflux ratio R of between 0.5 and 5[, preferably between 1 and 2].

10. (Amended) The process as claimed in [any one of claims 1 to 6] claim 1, [characterized in that] wherein the detarring column or columns (1, 1') is/are scraped falling film devices.

Attachment to Preliminary Amendment dated July 25, 2001

11. (Amended) The process as claimed in [any one of claims 1 to 10] claim 1, [characterized in that] wherein the crude mixture comprises, with respect to the total mixture:

- from 20 to 60%[, in particular from 30 to 50%,] by weight of hydroquinone,
- from 2 to 20%[, in particular from 2 to 15%,] by weight of resorcinol,
- from 0 to 20%[, in particular from 5 to 15%,] by weight of catechol, and
- the remainder being formed of various compounds[, essentially] comprising tars.

13. (Amended) The plant as claimed in claim 12, [characterized in that it] which additionally comprises:

- a detarring column (1) designed to produce, at the column top, a detarred fraction and, at the bottom of the column, a tar-rich fraction
- optionally at least one other distillation column (11) fed with the tar-rich fraction originating from the preceding column (1) and designed to produce, at the column top, a detarred fraction and, at the bottom, a tar-rich fraction,

the top fraction or fractions of these columns being used to feed column (I) or (II).

14. (Amended) The plant as claimed in claim 12 [or 13], [characterized in that] wherein the column (II) is designed to result in a resorcinol-rich fraction comprising:

- from 75 to 95%[, preferably from 85 to 92%, of] resorcinol, and
- from 5 to 25%[, preferably from 8 to 15%, of] hydroquinone.

Attachment to Preliminary Amendment dated July 25, 2001

15. (Amended) The plant as claimed in [any one of claims 12 to 14] claim 12, [characterized in that] wherein the column (III) is designed to result in a hydroquinone-rich fraction comprising:

- from 75 to 98%[, preferably from 85 to 97.5%, of] hydroquinone, and
- from 2 to 25%[, preferably from 2.5 to 15%, of] resorcinol.

16. (Amended) The plant as claimed in [any one of claims 12 to 15] claim 12, [characterized in that] wherein the refining device or -devices are drainers.

17. (Amended) The plant as claimed in [any one of claims 12 to 16] claim 12, [characterized in that] wherein the distillation column (I) has the following specifications:

- number of theoretical stages: from 5 to 40[, preferably from 10 to 30]; and
- reflux ratio R of between 1 and 10[, preferably between 2 and 5].

18. (Amended) The plant as claimed in [any one of claims 12 to 17] claim 12, [characterized in that] wherein the distillation column (II) has the following specifications:

- number of theoretical stages: from 10 to 85[, preferably from 15 to 40; and

reflux ratio R of between 1 and 35[, preferably between 5 and 25].

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19. (Amended) The plant as claimed in [any one of claims 12 to 18] claim 12, [characterized in that] wherein the distillation column (III) is a scraped falling film device or a distillation column having the following specifications:

- number of theoretical stages: from 1 to 10[, preferably from 1 to 5], and
- reflux ratio R of between 0.5 and 5[, preferably between 1 and 2].

20. (Amended) The plant as claimed in [any one of claims 12 to 19] claim 12, [characterized in that] wherein the detarring column or columns (1, 1') is/are scraped falling film devices.

Process and plant for the separation and purification of diphenols in the phenol and phenol derivatives industry

The present invention relates to a process for the separation and purification of crude mixtures essentially comprising hydroquinone and resorcinol, optionally tars and optionally catechol, in order to extract therefrom first the hydroquinone and secondly the resorcinol, and the catechol, when it is present, and optionally to purify these various compounds. It also relates to the plants which allow this process to be implemented.

The phenol and phenol derivatives industry generates large volumes of byproducts comprising, among a great variety of tars, the para, ortho and meta derivatives of dihydroxybenzene. They are hydroquinone (para compound: 1,4-dihydroxybenzene), catechol or pyrocatechin (ortho compound: 1,2-dihydroxybenzene) and resorcinol or resorcin (meta compound: 1,3-dihydroxybenzene).

These three compounds have an added value but their extraction from such complex mixtures is not without presenting problems of a technical nature and an economic nature. Moreover, hydroquinone and resorcinol are isomers which are particularly difficult to separate.

FR-A-2 467 185 discloses a process for the separation and purification of resorcinol and hydroquinone involving stages of distillation and of recrystallization by using a solvent such as water or an organic solvent. According to one alternative form, this process provides distillation stages using steam for entraining the hydroquinone in the form of hydroquinone vapor. This process uses a third solvent which subsequently has to be removed, which requires additional stages and devices, for example for

filtration and for drying, and optionally for reprocessing or recycling the solvent.

An object of the present invention, which relates in particular to the separation and the purification of diphenols in the phenol and phenol derivatives industry, is to provide an appropriate method and plant which make it possible to separate and to purify, under favorable economical conditions, hydroquinone and resorcinol from a crude mixture.

Another object of the invention is to make possible the separation and the purification of first hydroquinone and secondly resorcinol from a crude mixture comprising other compounds, in particular tars, and/or optionally catechol, and also to separate and purify the catechol optionally present.

Another object of the invention is to provide such a process which can be operated largely continuously.

Yet another object of the invention is to provide such a process and plant which make it possible to obtain hydroquinone, resorcinol and catechol having a high purity, in particular of greater than 98%, preferably than 99%, indeed even greater than or equal to 99.5%.

Yet another object of the invention is to provide such a process which does not require the use of a third solvent.

These objects are achieved in accordance with the invention by a process for the purification of a crude mixture comprising hydroquinone and resorcinol, optionally tars, and optionally catechol, in which process the crude mixture is subjected to a series of distillation stages, preferably carried out continuously, comprising:

(i) an optional first distillation stage (I) designed to produce catechol as distillation top product; this stage is carried out when the crude mixture comprises catechol, in particular

when the content of catechol in the crude mixture exceeds 2% inclusive,

(ii) the distillation bottom product obtained under (i) where the crude mixture in the absence of stage (I) is subjected to a distillation stage (II) designed to produce, as distillation top product, a resorcinol-rich fraction comprising resorcinol, essentially, and hydroquinone,

(iii) the distillation bottom product obtained under (ii) is subjected to a distillation stage (III) designed to produce, as distillation top product, a hydroquinone-rich fraction comprising hydroquinone, essentially, and resorcinol,

and then the hydroquinone-rich fraction and/or the resorcinol-rich fraction is/are subjected to a refining stage (IV, V) in order to extract the hydroquinone and/or the resorcinol.

In order to improve the yield for the recovery of hydroquinone from the crude mixture, it is preferable to precede stages (I) and/or (II) by at least one predistillation "detarring" stage (1) which makes it possible to remove the tars as distillation bottom product. It is even preferable then to redistil this distillation bottom product in at least one second preliminary detarring stage (1') and to recover the distillation top product, capable of comprising a certain amount of the desired compounds. The distillation [lacuna] or the two (or more) distillation top products thus obtained are conveyed as feed mixture to stage (I), if such a stage is provided, or stage (II), in the contrary case. More preferably, these preliminary stages are carried out continuously with the distillation stages which follow.

The mixtures to which the process applies are mainly those comprising in particular, with respect to the total mixture:

- from 20 to 60%, in particular from 30 to 50%, by weight of hydroquinone,
- from 2 to 20%, in particular from 2 to 15%, by weight of resorcinol,
- from 0 to 20%, in particular from 5 to 15%, by weight of catechol,
- the remainder being formed of various compounds, essentially tars.

The "detarring" distillation stages (1, 1') can be carried out with scraped falling film devices of conventional design or short path devices. However, the use of multistage columns is not ruled out (see, e.g., column (III)). The aim is simply to remove as much as possible of the tars without a significant loss of the desired compounds.

If stages (1 and 1') are not provided, it is preferable to use columns (I) and (II) with antifouling packings in order to limit the fouling thereof by the tars. Such packings are fully known to a person skilled in the art.

Stage (I) is targeted simply at extracting the catechol and thus at obtaining, as top product, catechol with a purity which is as high as possible. The aim in particular is to obtain a fraction comprising at least 98%, preferably at least 99%, of catechol.

The term "rich" as used above for stages (II) and (III) is understood to mean that the compound targeted is the major component, the other compound being a minor component but present in a sufficient amount to subsequently make possible the refining. A person skilled in the art is entirely in a position to determine by routine tests the ranges of ratios, basing himself on the crystallization curve of a resorcinol/hydroquinone mixture, in order to determine the ratios corresponding to the range of the eutectics. From this information, by varying the operating parameters of the columns, it is possible to achieve conditions such that

the rich fractions have a ratio which appears on either side of this range, as is known per se, which will allow the subsequent implementation of the refining.

The operating conditions of stages (II) and (III) are thus related. Each is targeted at the production, as distillation top product (as column top product), of a hydroquinone/resorcinol mixture which is compatible with the subsequent refining stage.

It is thus preferable for stage (III) to result in a mixture comprising:

- from 75 to 95%, preferably from 85 to 92%, of resorcinol,
- from 5 to 25%, preferably from 8 to 15%, of hydroquinone.

(Possible residues of other compounds, e.g. catechol, which remain minor components, are not taken into account).

These operating conditions make it possible to ensure, during stage (III), the production as distillation top product of a mixture comprising in particular:

- from 75 to 98%, preferably from 85 to 97.5%, of hydroquinone,
- from 2 to 25%, preferably from 2.5 to 15%, of resorcinol.

(Here again, possible residues of other compounds which may be present in negligible amounts are not taken into account).

From this information, a person skilled in the art is fully in a position to choose the means to be employed according to the starting mixture. The following should simply be noted. The size (in particular the diameter) of the distillation columns depends on the circulating stream and on the internal pressure. They will thus be dimensioned mainly according to the flow rate of the mixture to be treated. The internal parameter which is the number of theoretical stages is determined in particular by the

composition (ratios) of the entering mixture and the purity or the composition of the mixture which has to be obtained as distillation top product and as distillation bottom product. It will be specified that the columns may without distinction be packed with plates or with stacked packing, as is fully known to a person skilled in the art. The plant having been determined, a person skilled in the art adjusts the operating parameters of the columns.

Thus, the distillation column (I) can advantageously but not limitingly be a column having the following specifications:

- number of theoretical stages: from 5 to 40, preferably from 10 to 30;
- reflux ratio R of between 1 and 10, preferably between 2 and 5.

The distillation column (II) can advantageously but not limitingly be a column having the following specifications:

- number of theoretical stages: from 10 to 85, preferably from 15 to 40,
- reflux ratio R of between 1 and 35, preferably between 5 and 25.

The distillation column (III) can very simply be a column of type (1) or alternatively a column having the following specifications:

- number of theoretical stages: from 1 to 10, preferably from 1 to 5,
- reflux ratio R of between 0.5 and 5, preferably between 1 and 2.

The refining is carried out batchwise using devices which make possible liquid/solid separation (draining, zone melting) and which are dimensioned according to the volume to be treated and their number. The choice of the type of device is not critical either. They can, for example, be conventional drainers or other refining devices, for example those sold under the name Proapt (registered trademark). It is possible,

for example, to use drainers of the type with a vertical cylindrical tubular exchanger.

The treatment of the rich fractions in these devices is carried out essentially according to the four following phases:

- phase 1 corresponds to the slow crystallization of the charged mixture
- phase 2 corresponds to the cold draining of the eutectic (resorcinol and hydroquinone mixture)
- phase 3 corresponds to the hot draining recovered during the reheating phase until the desired purity is obtained
- phase 4 corresponds to the melting-recovery of the pure product.

The production of fractions with substantially constant compositions also makes it possible to automate the progress of this refining.

The resorcinol-rich fraction is conveyed to one or more refining device(s). Before phase 1, the device is heated above the melting point of resorcinol (11°C), i.e., for example, between 115 and 120°C.

During phase 1, the body of material is cooled, e.g. to a temperature of between 40 and 90°C, over several hours, e.g. over from 5 to 15 h, which results in the slow crystallization of the charged mixture.

After phase 1, the product which has remained liquid is withdrawn from the device (phase 2) before passing to phase 3.

Phase 3 consists of the slow reheating of the refining device, optionally begun during phase 2, e.g. up to a temperature of between 109 and 111°C, over several hours, e.g. over from 8 to 15 h. The end of phase 3, which conditions the purity of the product, can be determined either by measuring the crystallization point or by any other physiochemical analytical technique.

Phase 4 provides for heating of the device to a temperature greater than 115°C, so as to melt the

resorcinol, which is withdrawn in the molten state.

The hydroquinone-rich fractions are treated in the same way. The treatment follows the same phases, apart from the heating/cooling temperatures and times. By way of example:

- preheating between 175 and 180°C
- phase 1, cooling between 90 and 130°C
- phase 1, duration between 5 and 15 h
- phase 3, heating between 170 and 173°C
- phase 3, duration between 8 and 24 h
- phase 4, heating above 178°C.

The eutectic fractions recovered during the refining can be recycled as a mixture or separately with the hot drainings, preferably in stages (II) and/or (III). It is possible to be induced to recycle them in stage (I), if need be.

Another subject matter of the present invention is a plant which makes possible the implementation of the process described above, comprising:

(i) an optional distillation column (I) designed to produce catechol at the column top,

(ii) a distillation column (II), the inlet of which is connected to the bottom of column (I) or receives the crude mixture in the absence of column (I), this column (II) being designed to produce, at the column top, a resorcinol-rich fraction comprising resorcinol, essentially, and hydroquinone,

(iii) a distillation column (III), the inlet of which is connected to the bottom of column (II), this column (III) being designed to produce, at the column top, a hydroquinone-rich fraction comprising hydroquinone, essentially, and resorcinol,

(iv) one or more refining devices (IV, V) for providing for the refining of the hydroquinone-rich fraction and/or the

resorcinol-rich fraction in order to extract hydroquinone and/or resorcinol respectively.

In accordance with the preferred embodiment of the invention, this plant additionally comprises:

- a detarring column (1) designed to produce, at the column top, a detarred fraction and, at the bottom of the column, a tar-rich fraction
- optionally at least one other distillation column (1') fed with the tar-rich fraction originating from the preceding column (1) and designed to produce, at the column top, a detarred fraction and, at the bottom, a tar-rich fraction,

the top fraction or fractions of these columns being used to feed column (I) or (II).

The other information and characteristics given above with respect to the process apply directly to the plant according to the invention.

The invention will now be described in more detail with the help of embodiments taken as nonlimiting examples and with reference to the drawing, in which:

- Figure 1 shows the diagram of a first plant in accordance with the invention
- Figure 2 shows the diagram of a second plant in accordance with the preferred embodiment of the invention.

EXAMPLE 1 (Figure 1):

1st Distillation column (I):

n (number of theoretical stages) = 30

R (reflux ratio) = 2.7

Column top temperature = 176.4°C

Pressure = 100 mmHg, i.e. 13 332 Pa.

This column (I) is fed continuously with a flow rate of 25.5 kg/h of a mixture to be treated comprising:

- approximately 50% hydroquinone, i.e. approximately

12.75 kg/h

- approximately 15% catechol, i.e. approximately 3.8 kg/h
- approximately 10% resorcinol, i.e. approximately 2.55 kg/h
- approximately 25% tars, i.e. approximately 6.4 kg/h.

A flow rate of approximately 3.8 kg/h is obtained at the column top, which flow rate comprises:

- approximately 99.5% catechol
- approximately 800 ppm hydroquinone
- approximately 40 ppm resorcinol.

A flow rate of approximately 21.7 kg/h is obtained at the column bottom, which flow rate comprises:

- approximately 58.9% hydroquinone (approximately 12.75 kg/h)
- approximately 11.7% resorcinol (approximately 2.55 kg/h)
- approximately 180 ppm catechol
- approximately 29.4% tars (approximately 6.4 kg/h).

2nd Distillation column (II):

n = 30

R = 10

Column top temperature: 210°C

Pressure: = 100 mmHg, i.e. 13 332 Pa.

It is fed continuously with the bottom product from the 1st column at a flow rate of approximately 21.7 kg/h.

A flow rate of approximately 2.56 kg/h of a resorcinol-rich fraction is obtained at the top, which fraction comprises:

- approximately 90% resorcinol (approximately 2.3 kg/h)
- approximately 10% hydroquinone (approximately 0.26 kg/h,
- approximately 1 200 ppm catechol.

A flow rate of approximately 19.14 kg/h of a

mixture is obtained at the bottom, which mixture comprises:

- approximately 65.3% hydroquinone (approximately 12.49 kg/h)
- approximately 1.3% resorcinol (approximately 0.25 kg/h)
- approximately 33.4% tars (approximately 6.4 kg/h).

3rd (Distillation) detarring column (III):

Detarring column: scraped falling film device
Column top temperature: 217°C
Pressure: 100 mmHg, i.e. 13 332 Pa.

This column is fed continuously with the bottom product from the 2nd column at a flow rate of approximately 19.14 kg/h

A flow rate of approximately 9.64 kg/h of a hydroquinone-rich fraction is obtained at the top, which fraction comprises:

- approximately 97.4% hydroquinone (approximately 9.39 kg/h)
- approximately 2.6% resorcinol (approximately 0.25 kg/h)

A flow rate of approximately 9.5 kg/h of a mixture is obtained at the column bottom, which mixture comprises:

- approximately 32.6% hydroquinone (approximately 3.1 kg/h)
- approximately 67.4% tars (approximately 6.4 kg/h).

The column bottom product can optionally be redistilled on a detarring column.

Refining:

The refining makes it possible to obtain the pure products from the rich fractions. Drainers of the type with a vertical cylindrical tubular exchanger were used. Similar results will be obtained with other types of devices.

The operating method is as follows:

a) for the hydroquinone-rich fraction:

- Charging: before the charging of approximately 180 kg of hydroquinone-rich fractions, the drainer (V) is preheated to a temperature greater than the melting point of hydroquinone, in this instance to approximately 180°C.
- Cooling: the body of material is slowly cooled by circulation of water to a temperature of approximately 120°C (cooling time approximately 10 h).
- Recovery of the eutectic fraction: the eutectic fraction, which is also known as cold drainings, corresponds to the uncrystallized part of the mixture at the end of cooling and is a mixture of resorcinol and hydroquinone. In the case of these drainers, this fraction can be recovered by simple gravimetric flow and collected in a tank provided for this purpose. This phase lasts approximately 12 hours and takes place with slow reheating of the drainer.
- The reheating of the drainer is continued in order to carry out the hot draining phase. The end of the phase of recovery of the hot drainings is determined by the measurement of the crystallization point of the product which seeps out during this heating phase. This fraction is recovered by simple gravimetric flow and is collected in a tank provided for this purpose. This fraction can either be recycled to the following refining operation or mixed with the cold draining fraction and recycled to the distillation.
- Recovery of the pure hydroquinone: when the crystallization point (171°C) is reached, the flow of the hot drainings is interrupted and the drainer is heated to a temperature of 180°C in order to melt all the hydroquinone. Approximately 65 kg of hydroquinone are recovered with an assay of greater than or equal to 99.5%.

b) For the resorcinol-rich fraction: the processing is carried out in the same way as under a) with the drainer (IV), apart from the essential difference that this time it is the melting temperature of resorcinol which is taken into account, which temperature is 111°C. The heating temperatures are consequently modified.

Charging temperature 120°C

Cooling to 60°C over approximately 10 h

Recovery of the cold draining fraction over approximately 10 h

Reheating from 60 to 110.5°C, the end of this reheating being determined by the measurement of the crystallization point, which determines the final purity of the product.

Heating to 120°C in order to recover the resorcinol: 65 kg with a purity of greater than or equal to 99%.

EXAMPLE 2: (Figure 2)

In comparison with example 1, two detarring columns (1 and 1') are added upstream of the distillation column (I) to remove at the start the tars present. The first (1) of these columns is fed with the mixture to be treated and the second (1') with the bottom product from the preceding column (1). The streams originating from the two column tops feed the 1st column (I) according to example 1.

Detarring columns

Scraped falling film devices

Column top temperature: 174°C

Pressure: 10 mmHg, i.e. 1 333.2 Pa.

The column (1) is fed continuously with a flow rate of 35 kg/h with a mixture to be treated comprising:

- approximately 45% hydroquinone, i.e. approximately 15.75 kg/h
- approximately 7% catechol, i.e. approximately 2.45 kg/h

- approximately 3% resorcinol, i.e. approximately 1.05 kg/h
- approximately 45% tars, i.e. approximately 15.75 kg/h.

The top products from the two detarring columns are combined and produce a flow rate of approximately 18.9 kg/h of a detarred fraction comprising:

- approximately 2.45 kg/h catechol
- approximately 15.3 kg/h hydroquinone
- approximately 1.05 kg/h resorcinol
- approximately 0.1 kg/h tars.

A flow rate of approximately 16.1 kg/h of a tar-rich fraction is obtained at the bottom of the column (1'), which fraction comprises:

- approximately 15.65 kg/h tars
- approximately 0.45 kg/h hydroquinone

Distillation column (I):

n (number of theoretical stages) = 30
R (reflux ratio) = 2.7
Column top temperature = 134°C
Pressure = 10 mmHg, i.e. 1 333.2 Pa.

This column (I) is fed continuously with the flow rate of 18.9 kg/h originating from the detarring.

A flow rate of approximately 2.45 kg/h is obtained at the column top, which flow rate comprises:

- approximately 99.5% catechol
- approximately 800 ppm hydroquinone
- approximately 40 ppm resorcinol.

A flow rate of approximately 16.45 kg/h is obtained at the column bottom, which flow rate comprises:

- approximately 15.3 kg/h hydroquinone
- approximately 1.05 kg/h resorcinol
- approximately 180 ppm catechol
- approximately 0.1 kg/h tars.

Distillation column (II):

n = 30

R = 10

Column top temperature: 170°C

Pressure: 10 mmHg, i.e. 1 333.2 Pa.

It is fed continuously with the bottom product from the column (I) at a flow rate of approximately 16.45 kg/h.

A flow rate of approximately 0.75 kg/h of a resorcinol-rich fraction is obtained at the top, which fraction comprises:

- approximately 0.65 kg/h resorcinol
- approximately 0.1 kg/h hydroquinone
- approximately 1 200 ppm catechol.

A flow rate of approximately 15.7 kg/h of a mixture is obtained at the bottom, which mixture comprises:

- approximately 15.2 kg/h hydroquinone
- approximately 0.4 kg/h resorcinol
- approximately 0.1 kg/h tars.

(Distillation) detarring column (III):

Detarring column: scraped falling film device

Column top temperature: 174.5°C

Pressure: 10 mmHg, i.e. 1 333.2 Pa.

This column is fed continuously with the bottom product from the column (II) at a flow rate of approximately 15.7 kg/h.

A flow rate of approximately 15.2 kg/h of a hydroquinone-rich fraction is obtained at the top, which fraction comprises:

- approximately 14.8 kg/h hydroquinone
- approximately 0.4 kg/h resorcinol.

A flow rate of approximately 0.5 kg/h of a mixture is obtained at the column bottom, which mixture comprises:

- approximately 0.4 kg/h hydroquinone
- approximately 0.1 kg/h tars.

Refining:

The refining is carried out as in example 1.

It must be clearly understood that the invention defined by the appended claims is not limited to the specific embodiments indicated in the above description but encompasses the alternative forms thereof which depart neither from the scope nor from the spirit of the present invention.

CLAIMS

1. A process for separation and purification of a crude mixture comprising hydroquinone and resorcinol, optionally tars, and optionally catechol, in which process the crude mixture is first of all subjected to a series of distillation stages comprising:

(i) an optional distillation stage (I) designed to produce catechol as distillation top product,

(ii) the distillation bottom product obtained under (i) or the crude mixture in the absence of stage (I) is subjected to a distillation stage (II) designed to produce, as distillation top product, a resorcinol-rich fraction comprising resorcinol, essentially, and hydroquinone,

(iii) the distillation bottom product obtained under (ii) is subjected to a distillation stage (III) designed to produce, as distillation top product, a hydroquinone-rich fraction comprising hydroquinone, essentially, and resorcinol,

and then the hydroquinone-rich fraction and/or the resorcinol-rich fraction is/are subjected to a refining stage (IV or V) in order to extract the hydroquinone and/or the resorcinol respectively.

2. The process as claimed in claim 1, characterized in that stage (I), when it is present, or stage (II) is preceded by at least one preliminary detarring stage (1, 1') designed to produce, as bottom product, a tar-rich fraction and, as top product, a detarred fraction which is used to feed stage (I) or stage (II).

3. The process as claimed in claim 2, characterized in that two predistillation stages (1, 1') are provided, the tar-rich bottom fraction from the first (1) being used to feed the second (1') and the

two detarred top fractions being used to feed stage (I) or (II).

4. The process as claimed in any one of claims 1 to 3, characterized in that stage (II) is designed to result in a resorcinol-rich fraction comprising:

- from 75 to 95%, preferably from 85 to 92%, of resorcinol,
- from 5 to 25%, preferably from 8 to 15%, of hydroquinone.

5. The process as claimed in any one of claims 1 to 4, characterized in that stage (III) is designed to result in a hydroquinone-rich fraction comprising:

- from 75 to 98%, preferably from 85 to 97.5%, of hydroquinone,
- from 2 to 25%, preferably from 2.5 to 15%, of resorcinol.

6. The process as claimed in any one of claims 1 to 5, characterized in that the refining of the rich fractions is carried out on drainers.

7. The process as claimed in any one of claims 1 to 6, characterized in that the distillation column (I) has the following specifications:

- number of theoretical stages: from 5 to 40, preferably from 10 to 30;
- reflux ratio R of between 1 and 10, preferably between 2 and 5.

8. The process as claimed in any one of claims 1 to 6, characterized in that the distillation column (II) has the following specifications:

- number of theoretical stages: from 10 to 85, preferably from 15 to 40;
- reflux ratio R of between 1 and 35, preferably between 5 and 25.

9. The process as claimed in any one of claims 1 to 6, characterized in that the distillation column (III) is a scraped falling film device or a distillation column having the following specifications:

- number of theoretical stages: from 1 to 10, preferably from 1 to 5,
- reflux ratio R of between 0.5 and 5, preferably between 1 and 2.

10. The process as claimed in any one of claims 1 to 6, characterized in that the detarring column or columns (1, 1') is/are scraped falling film devices.

11. The process as claimed in any one of claims 1 to 10, characterized in that the crude mixture comprises, with respect to the total mixture:

- from 20 to 60%, in particular from 30 to 50%, by weight of hydroquinone,
- from 2 to 20%, in particular from 2 to 15%, by weight of resorcinol,
- from 0 to 20%, in particular from 5 to 15%, by weight of catechol,
- the remainder being formed of various compounds, essentially tars.

12. A plant for the separation and purification of a crude mixture comprising hydroquinone, resorcinol, tars and optionally catechol, comprising:

(i) an optional distillation column (I) designed to produce catechol at the column top,

(ii) a distillation column (II), the inlet of which is connected to the bottom of column (I) or receives the crude mixture in the absence of column (I), this column (II) being designed to produce, at the column top, a resorcinol-rich fraction comprising resorcinol, essentially, and hydroquinone,

(iii) a distillation column (III), the inlet of which is connected to the bottom of column (II), this column (III) being designed to produce, at the column top, a hydroquinone-rich fraction comprising hydroquinone, essentially, and resorcinol,

(iv) one or more refining devices (IV, V) for

providing for the refining of the hydroquinone-rich fraction and/or the resorcinol-rich fraction in order to extract hydroquinone and/or resorcinol respectively.

13. The plant as claimed in claim 12, characterized in that it additionally comprises:

- a detarring column (1) designed to produce, at the column top, a detarred fraction and, at the bottom of the column, a tar-rich fraction
- optionally at least one other distillation column (1') fed with the tar-rich fraction originating from the preceding column (1) and designed to produce, at the column top, a detarred fraction and, at the bottom, a tar-rich fraction,

the top fraction or fractions of these columns being used to feed column (I) or (II).

14. The plant as claimed in claim 12 or 13, characterized in that the column (II) is designed to result in a resorcinol-rich fraction comprising:

- from 75 to 95%, preferably from 85 to 92%, of resorcinol,
- from 5 to 25%, preferably from 8 to 15%, of hydroquinone.

15. The plant as claimed in any one of claims 12 to 14, characterized in that the column (III) is designed to result in a hydroquinone-rich fraction comprising:

- from 75 to 98%, preferably from 85 to 97.5%, of hydroquinone,
- from 2 to 25%, preferably from 2.5 to 15%, of resorcinol.

16. The plant as claimed in any one of claims 12 to 15, characterized in that the refining device or devices are drainers.

17. The plant as claimed in any one of claims 12 to 16, characterized in that the distillation column (I) has the following specifications:

- number of theoretical stages: from 5 to 40,

preferably from 10 to 30;

- reflux ratio R of between 1 and 10, preferably between 2 and 5.

18. The plant as claimed in any one of claims 12 to 17, characterized in that the distillation column (II) has the following specifications:

- number of theoretical stages: from 10 to 85, preferably from 15 to 40;

reflux ratio R of between 1 and 35, preferably between 5 and 25.

19. The plant as claimed in any one of claims 12 to 18, characterized in that the distillation column (III) is a scraped falling film device or a distillation column having the following specifications:

- number of theoretical stages: from 1 to 10, preferably from 1 to 5,
- reflux ratio R of between 0.5 and 5, preferably between 1 and 2.

20. The plant as claimed in any one of claims 12 to 19, characterized in that the detarring column or columns (1, 1') is/are scraped falling film devices.

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Bureau international

DEMANDE INTERNATIONALE PUBLIEE EN VERTU DU TRAITE DE COOPERATION EN MATIERE DE BREVETS (PCT)

(51) Classification internationale des brevets 7 : C07C — A2

(11) Numéro de publication internationale: WO 00/43334

(43) Date de publication internationale: 27 juillet 2000 (27.07.00)

(21) Numéro de la demande internationale: PCT/FR00/00166

(22) Date de dépôt international: 25 janvier 2000 (25.01.00)

(30) Données relatives à la priorité:
99/00908 25 janvier 1999 (25.01.99) FR

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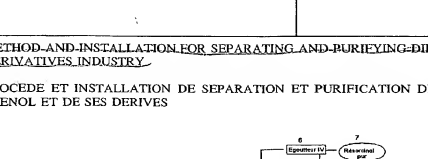
(81) Etats désignés: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, brevet ARIPO (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), brevet eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), brevet OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Publiée

Sans rapport de recherche internationale, sera republiée dès réception de ce rapport.

(54) Title: METHOD AND INSTALLATION FOR SEPARATING AND PURIFYING DIPHENOLS IN THE PHENOL AND PHENOL DERIVATIVES INDUSTRY

(54) Titre: PROCEDE ET INSTALLATION DE SEPARATION ET PURIFICATION DES DIPHENOLS DANS L'INDUSTRIE DU PHENOL ET DE SES DERIVES



(57) Abstract

A method and installation for separating and purifying a crude mixture containing hydroquinone, resorcinol and possibly tars and/or catechol, comprising the following steps: – a possible distillation stage (I) in order to obtain a catechol head, – the foot (I) or crude mixture undergoes distillation (II) in order to obtain a fraction that is rich in resorcinol, – the foot of (II) undergoes distillation (III) in order to obtain a fraction that is rich in hydroquinone, whereupon said rich fractions are refined (IV or V). Preferably, one or several stages in which tar is removed (I,1') precede stage (I) or (II).

(57) Abrégé

Procédé et installation de séparation et purification d'un mélange brut contenant hydroquinone, résorcinol, éventuellement goudrons et/ou catéchol, comprenant: une éventuelle étape de distillation (I) conçue pour obtenir du catéchol en tête; le pied de (I), ou le mélange brut, est soumis à une étape de distillation (II) conçue pour obtenir en tête une fraction riche en résorcinol; le pied de (II) est soumis à une étape de distillation (III) conçue pour obtenir en tête une fraction riche en hydroquinone, puis on soumet ces fractions riches à du raffinage (IV ou V). On fait de préférence précéder l'étape (I) ou (II) d'une ou plusieurs étapes de dégoudronnage (1, 1').

WO 00/43334 PCT/FR00/00166

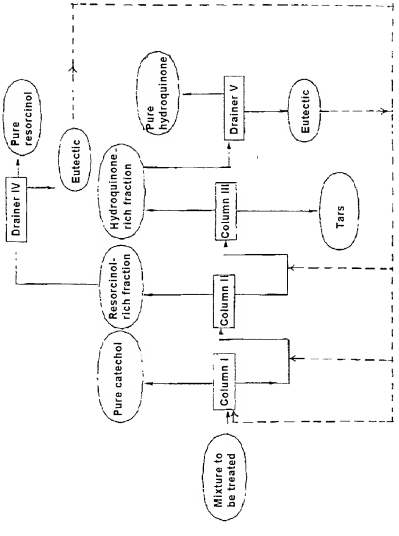


Fig.1

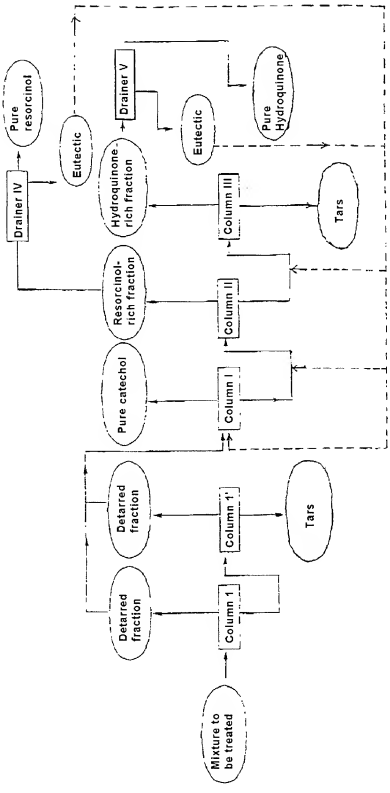

Mixture to be treated
Column 1
Detarred fraction
Column 1'
Tars
Detarred fraction
Column I
Pure catechol
Column II
Resorcinol-rich fraction
Column III
Tars
Hydroquinone-rich fraction
Eutectic
Drainer V
Pure Hydroquinone
Eutectic
Drainer IV
Pure resorcinol

Fig.2

SCANNED;# 8

COMBINED DECLARATION AND POWER OF ATTORNEY FOR UTILITY PATENT APPLICATION	Attorney's Docket No.

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I BELIEVE I AM THE ORIGINAL, FIRST AND SOLE INVENTOR (if only one name is listed below) OR AN ORIGINAL, FIRST AND JOINT INVENTOR (if more than one name is listed below) OF THE SUBJECT MATTER WHICH IS CLAIMED AND FOR WHICH A PATENT IS SOUGHT ON THE INVENTION ENTITLED:

Method and installation for separating and purifying in the phenol and phenol derivatives industry

the specification of which

(check one)

☐ is attached hereto;

☒ was filed on January 25, 2000 as

Application No. PCT/FR00/00166

and was amended on ______________________;
(if applicable)

I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE;

I ACKNOWLEDGE THE DUTY TO DISCLOSE TO THE OFFICE ALL INFORMATION KNOWN TO ME TO BE MATERIAL TO PATENTABILITY AS DEFINED IN TITLE 37, CODE OF FEDERAL REGULATIONS, Sec. 1.56 (as amended effective March 16, 1992);

I do not know and do not believe the said invention was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to said application; that said invention was not in public use or on sale in the United States of America more than one year prior to said application; that said invention has not been patented or made the subject of an inventor's certificate issued before the date of said application in any country foreign to the United States of America on any application filed by me or my legal representatives or assigns more than twelve months prior to said application;

I hereby claim foreign priority benefits under Title 35, United States Code Sec. 119 and/or Sec. 365 of any foreign application(s) for patent or inventor's certificate as indicated below and have also identified below any foreign application for patent or inventor's certificate on this invention having a filing date before that of the application(s) on which priority is claimed:

COMBINED DECLARATION AND POWER OF ATTORNEY

Attorney's Docket No.

COUNTRY/INTERNATIONAL	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED
FRANCE	FR 99 00908	25.01. 1999	YES X NO_
			YES_ NO_

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Address all telephone calls to: ______________________ at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF SOLE OR FIRST INVENTOR	SIGNATURE	DATE
Jacques BOURDON	[signature]	19.11.2001
RESIDENCE: 12, allée de la Roseraie - 69110 SAINTE FOY LES LYON/FRANCE FRX		CITIZENSHIP: French
POST OFFICE ADDRESS: same as above		
FULL NAME OF SECOND JOINT INVENTOR, IF ANY	SIGNATURE	DATE
Daniel CLERIN	[signature]	19.11.2001
RESIDENCE: 27, allée de la Pièce Rouge - 69230 SAINT GENIS LAVAL FRANCE FRX		CITIZENSHIP: French
POST OFFICE ADDRESS: same as above		

(10/00)

COMBINED DECLARATION AND POWER OF ATTORNEY	Attorney's Docket No.

FULL NAME OF THIRD JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF FOURTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF FIFTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF SIXTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF NINTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF TENTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		

COMBINED DECLARATION AND POWER OF ATTORNEY FOR UTILITY PATENT APPLICATION Supplemental Sheet	Attorney's Docket No.

Full Name of Additional Joint Inventor, If Any	
Signature	
Date	
Residence (City, State, Country)	
Citizenship	
Post Office Address	
Full Name of Additional Joint Inventor, If Any	
Signature	
Date	
Residence (City, State, Country)	
Citizenship	
Post Office Address	
Full Name of Additional Joint Inventor, If Any	
Signature	
Date	
Residence (City, State, Country)	
Citizenship	
Post Office Address	
Full Name of Additional Joint Inventor, If Any	
Signature	
Date	
Residence (City, State, Country)	
Citizenship	
Post Office Address	

ENDFIELD

(10/00)